eam and Deep UV Exposure of PMMA Based Resists - Identical or Different Chemical Behavior ?

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Abstract

The chemical reactions and the dissolution properties of homopolymeric PMMA and a P(MMA-co-MAA) copolymer were investigated during DUV (KrF, 248 nm) and e-beam exposure. The chain scission reaction was analyzed using GPC. The polymer degradation reaction is very similar at both exposure procedures. In both cases a bimodal and, later, a multimodal character of the molecular weight distribution is observed.

1. Introduction

Poly(methyl methacrylate) (PMMA) and its derivative Poly(methyl methacrylate -co- methacrylic acid) (P(MMA-co-MAA)), characterized by an approximately four times higher sensitivity[1], have been used as positive resists in electron beam lithography for a long time.[2] At deep UV exposure the PMMA based resists show a low sensitivity as a consequence of the low absorptivity (e.g. at λ_{ex} = 248 nm) and low chain scission efficiency[3]. Although, resists of the PMMA type require very high exposure doses, but, they produce images with excellent profiles.

The description of their lithographic performance has not only been done in experimental ways but calculations have been used, too. Only the use of correct parameters in these calculations provides the possibility to predict the lithographic behavior of the resist. Therefore, on one side investigations have been done to describe the chemical changes in PMMA and its derivative caused by irradiation with electron beam and deep UV light using spectroscopic and chromatographic methods. In both cases, the pathway of the polymer fragmentation is globally described by a Norrish Type I cleavage forming low molecular products. Details of the structure of products formed (bimodal molecular weight distribution[2]) show a more complex mechanism.

In this paper we check the applicability of the formula for the e-beam induced molecular weight change and the solubility rate on the basis of our experimental results. Proceeding from the independent experimental determination of both the solubility rate and the molecular weight on the deposited energy density we consider their correlation with each other and compare experimental data with calculated values for PMMA and P(MMA-co-MAA).

Compared with analogous experimental results for the deep UV degradation we show both similarities in the photochemistry at e-beam und DUV exposure and discuss different behavior.

2. Experimental

Resist preparation

Homopolymeric PMMA (Polyscience) and the photoresist ARP 610 (Allresist, Germany), dissolved in 2-methyl-glycol-acetate and 2-methyl-glycol, respectively, were spin-coated onto 4" silicon wafers to a thickness of about 1 µm and baked at 170°C for 1 hour.

E-beam exposure

The resist layers were electron beam exposed with an accelerating voltage of 20 kV over the whole wafer and different doses were applied (exposure tool ZBA 23, Jenoptik, Germany).

DUV exposure

The resist layers were DUV exposed using a KrF excimer laser EMG 104 MSC (Lambda Physik, Germany) and a DUV stepper NSR-2205EX12B (Nikon). The pulse energy used was 0.6 ... 3.9 mJ /cm^2 (EMG 104 MSC) and 0.23 mJ/cm^2 (DUV stepper). Different doses were applied controlled by the amount of pulses.

UV spectroscopy

The UV irradiation spectra of the exposed resist layers were measured on quartz substrates using a spectrometer U-3410 (Hitachi).

GPC measurements

To perform a GPC measurement the resist was completely removed from the wafers and dissolved in 2 ml tetrahydrofuran resp. methanol and analyzed by gel permeation chromatography (UV detection at 224 nm) using PL gel 10 mm mix B and PL gel 100 Å columns (Knauer), PMMA reference standards (Polyscience) and tetrahydrofuran as eluent. Thereafter molecular-weight distribution curves and the weight-average molecular weight $\overline{M}_w$ (formula 1) of each sample were determined using PSS Win GPC scientific V2.71 software.

$$\overline{M}_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \qquad (1)$$

Dissolution characteristics

The dissolution rate of ARP 610 depending on the deposited energy density was determined in a standard wet development process, using a developer containing methyl-isobutyl-ketone : isopropanol (MIBK/IPA) = 1:3 at a temperature of T = 22°C. The dissolution rate was determined by measuring the remaining resist thickness as a function of the exposure dose presented in Tab.I.

Deposited energy density E [eV/nm^3]	Dissolution rate [nm/s]
0.172	0.1064
0.345	0.1930
0.517	0.2820
0.690	0.3750
0.862	0.5000
1.293	1.0690
1.724	1.2586
2.155	2.3200
2.586	3.0680
3.017	5.3800
3.448	7.7270
3.879	10.2940
4.309	18.4700
5.171	29.2000

Table I. Dissolution rate of ARP 610 in MIBK/IPA at 22 °C

3. Results

Fig. 1 show the irradiation spectra of ARP 610 and PMMA at DUV exposure. The spectral changes at e-beam exposure are very similar.

GPC was used to investigate the dose dependence of the molecular weight distribution of PMMA and ARP 610 at e-beam and DUV exposure (λ_{ex} = 248 nm), respectively. The investigated range of e-beam dose was 0 µC/cm^2 ≤ D ≤ 150 µC/cm^2 (ARP 610, Fig. 2a), 0 µC/cm^2 ≤ D ≤ 300 µC/cm^2 (PMMA, Fig. 3a). The DUV exposure dose was 0 mJ/cm^2 ≤ D ≤ 36449 mJ/cm^2 (ARP 610, Fig. 2b) and 0 mJ/cm^2 ≤ D ≤ 200149 mJ/cm^2 (PMMA, Fig. 3b). Figs. 2 and 3 show that the maximum of the molecular weight distribution is shifted to lower molecular weights by increasing dose in all cases. A new character

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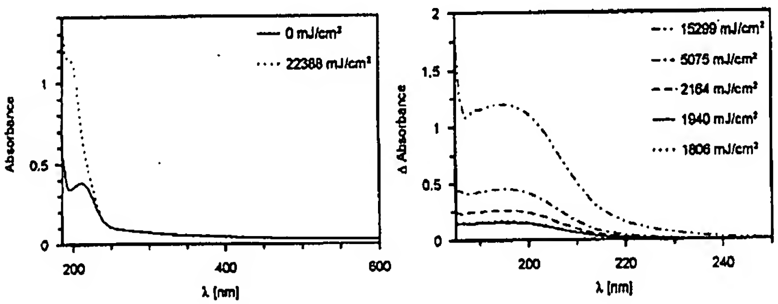


Fig. 1 Irradiation spectra during DUV exposure (laser: EMG 104 MSC; λ_{ex} = 248 nm; 10 Hz)
a: ARP 610 on quartz; b: PMMA on quartz; Δ Absorbance = Absorbance (t_{ex}) - Absorbance (t=0)

of the molecular weight distribution curve is observed with increasing dose starting with a value of D = 30μC/cm^2 (ARP 610, Fig. 2a and PMMA, Fig. 3a), D = 7687 mJ/cm^2 (ARP 610, Fig. 2b) and D = 12000 mJ/cm^2 (PMMA, Fig. 3b). A low molecular weight shoulder comes up with a maximum of about 2000 g/ mol. The molecular weight distribution becomes bimodal. In the range of higher doses > 60 μC/cm^2 and > 12000 mJ/cm^2, respectively, we do not observe a further shift of the higher weight maximum at M = 10000 g/mol, but its decrease to the credit of the lower weight fraction at M = 2000 g/mol.

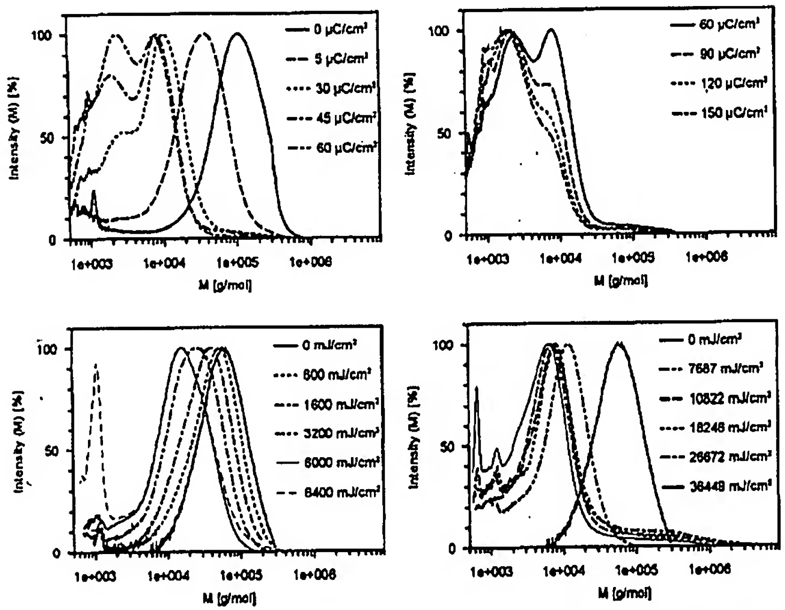


Fig. 2. GPC analytical data of ARP-610 after electron beam exposure (upper curves,Fig. 2a) and after DUV exposure (lower curves,Fig. 2b)

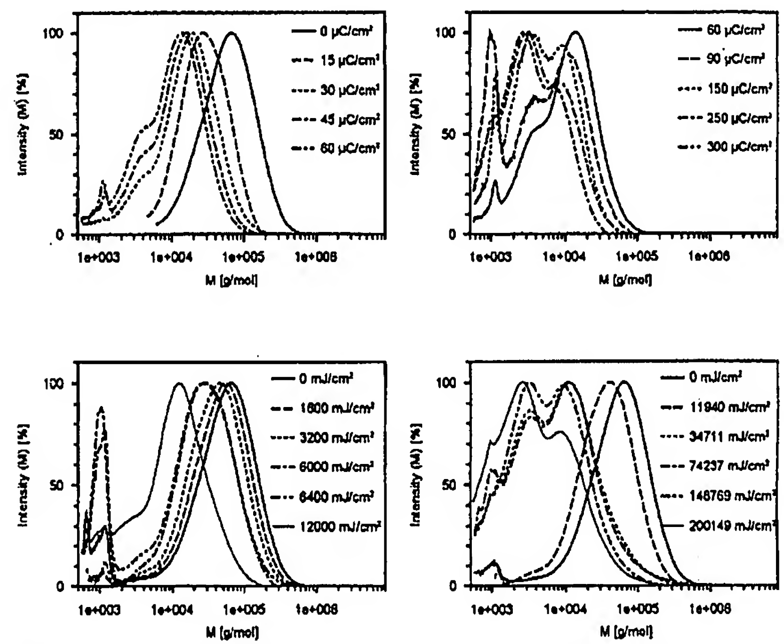


Fig. 3. GPC analytical data of PMMA after electron beam exposure (upper curves, Fig. 3a) and after DUV exposure (lower curves, Fig. 3b)

In addition the distribution becomes multimodal, and a corresponding increase of molecular weight fraction at M = 1000 g/mol and less is detected. In the case of the DUV exposed resist materials the formation of the weight fraction M = 1000 g/mol is stronger than for e-beam treated materials.
The bimodal and the multimodal distribution are the result of specific chain scission. Comparing the molecular weight of ARP 610 and PMMA, the chain scission efficiency is higher for ARP 610 than for PMMA.
To study the influence of chain scission of the resist during electron beam exposure on the lithographic behavior we measured the dissolution rate. Therefore, the dissolution rate of ARP 610 depending on the deposited energy density was determined in a standard wet development process. The conversion between the dose D [μC/cm^2] and the deposited energy density E [eV/nm^3] was made by calculations using Monte Carlo methods. The used substrate data are: density of the silicon layer: 2.33 g/cm^3, molecular weight: 28 g/mol. The following resist data were applied: density of ARP 610 1.04 g/cm^3, molecular weight of one monomer unit M_w = 98.4 g/mol [-$(C_5H_8O_2)_{0.74}$-$(C_4H_6O_2)_{0.26}$-corresponding to 74 % methyl methacrylate units and 26 % methacrylic acid units in ARP 610]. The results are presented in Tab.I.

4. Discussion

For a more comprehensive understanding of the dependence of molecular weight distribution on the dose at electron beam exposure calculations are performed using the GREENEICH model (formula 2)[4] of statistic chain scission of PMMA to check its applicability on the investigated resists ARP 610 and PMMA.

$$M_w = \frac{M_{w0}}{1+gEM_{w0}/\rho N_A} \qquad (2)$$

M_w: fragmented weight-average molecular weight; M_{w0}: weight-average molecular weight at $D = 0\ \mu C/cm^2$; g: scission efficiency; E: deposited energy density;
ρ: resist density (ρ(ARP 610) = 1.04 g/cm^3; ρ(PMMA) = 1.1 g/cm^3); N_A: Avogadro's number

Applying the GREENEICH model the following different scission efficiencies were calculated:
g (ARP 610) = $1.9 \cdot 10^{-2}$ events/eV and g (PMMA) = $5 \cdot 10^{-3}$ events/eV. The scission coefficient for ARP 610 corresponds to the value used by Greeneich. The g value of ARP 610 is about four times higher than that of PMMA, the influence of methacrylic acid units in ARP 610 leads to an increase of the scission efficiency.
Experimentally determined M_w/M_{w0} were compared to calculated M_w/M_{w0} data. The results are shown in Fig. 4. Calculated M_w/M_{w0} data are in agreement with experimental data at low deposited energy densities. At higher E values (ARP 610 > 4 eV/nm^3, PMMA > 8 eV/nm^3) increasing deposited energy densities cause increasing differences between experimental and calculated M_w/M_{w0} data. For both resists values for the weight-average molecular weight are found to be higher by experiment than by calculation.
The experimentally determined data of the DUV exposure are shown in Fig. 4, too.

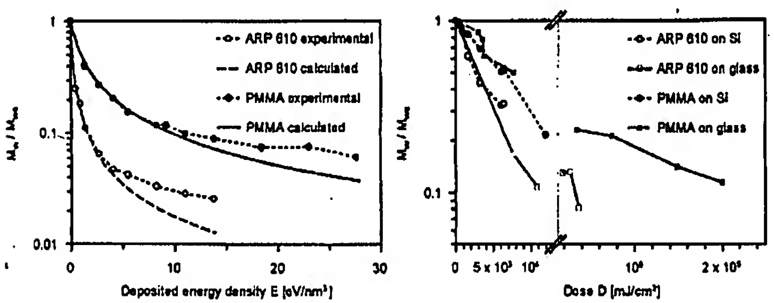
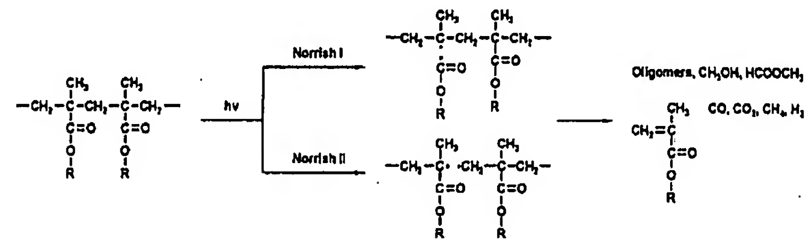


Fig. 4. Dependence of molecular weight distribution on exposure dose - left: e-beam; right: DUV

The mechanism of the e-beam and DUV induced chain scission is mainly characterized by a Norrish I cleavage. Beside the degradated polymer the volatile products shown in the scheme are detected using GC-MS (m/z = 41, 42, 43, 44, 45, 58, 59, 60, 61, 74). During both exposure procedures within the first period the molecular weight is shifted to lower values (Figs. 2 and 3) caused by the chain cleavage. The formation of the molecular weight fraction of about 1000 g/mol is favored during the second step of decomposition. The reason for the enhanced formation of these oligomers (≈ decamers) is still unknown. The degradation pathways during e-beam and DUV exposure are very similar.



Photochemical reactions in poly(methacrylic acid) derivative based polymers

5. Conclusion

The analytical data confirm the very similar chemical behavior of PMMA and P(MMA-co-MAA) at e-beam and DUV exposure. The chemical pathway is characterized by the chain scission (positive resist) and, more and more, by the favored formation of specific fractions (bimodal and multimodal distribution).

6. Acknowledgment

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